A STUDY OF FERRIC OXYACETATE HYDROSOLS

or

The Preparation, Precipitation and Aging of Ferric Oxyacetate Hydrosols, and the Application of the Quinhydrone Electrode to the Measurement of the pH of Iron Sols.

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
of Columbia University.

BY

FRED C. MABEE, A.M.

NEW YORK CITY
1927

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INTRODUCTION

Previous work in this laboratory on iron oxide sols by Thomas and Frieden[1], Frieden[2], and Hamburger[3] has dealt with the preparation and properties of sols stabilized with different stabilizing agents, particularly the halogen salts, ferric chloride and ferric bromide. The research which is presented in this paper deals with the behavior of the iron oxide sol* stabilized by ferric acetate.* The results provide fresh data on iron oxide sols, interesting theoretically in themselves, and also interesting because this sol is the first one containing an organic iron salt to be examined with the technique here described.

Almost all of the theoretical discussion connected with iron oxide sols has centered around the one which is stabilized by ferric chloride, originally described by Thomas Graham[4] in 1861. Six years earlier, however, Péan de St. Gilles had prepared and studied the properties of ferric acetate "solutions" (really sols). On adding sodium carbonate to his sols, a precipitate formed which he claimed had the composition "Fe_2O_3·

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* While this designation is conventional and is a heritage of the time when such sols were considered to be the oxide plus "impurities" it is not only no longer useful but actually misleading. Such sols will hereinafter be called ferric oxyacetate sols. Where the general type is mentioned the term "iron oxide sol" will be used for brevity.

HO." Having observed that boiling drives off acetic acid, and causes the sol particles to precipitate, he concluded that acetic acid was essential for stability under those circumstances.

A search of the literature was made to ascertain whether additional systematic studies of ferric oxyacetate sols has been made. While no systematic studies were discovered, there were, however, reports[6] of work done in repeating or extending parts of Péan de St. Gilles' experiments.

As regards the history of the development of modern theories of iron oxide sols it is not necessary here to do more than refer to the concise and excellent reviews contained in the theses of Frieden[2] and Hamburger[3].

II. PREPARATION OF THE SOLS

At the outset some experiments were made to duplicate Péan de St. Gilles method [5] of preparing sols from ferric acetate. His method consisted in heating and boiling solutions of ferric acetate for 25 to 30 hours, thus driving out part of the acetic acid formed by hydrolysis of the ferric acetate. His method also resulted, as pointed out by Frieden[1, 2] in dehydrating the colloidal particles, as compared to the hydrated particles of Graham's ferric oxychloride sols.

Another method tried out at the beginning was that of "hot dialysis." [7] Both the above methods, however, were abandoned in the early stages of the work, the chief reason being that it was desired to study the properties of the sol before any dehydration or coagulation due to heat had taken place. The method adopted was to dialyze the ferric acetate solution at laboratory temperature, for, once the unheated initial sols were prepared, and the initial analyses and measurements made, they could be heated at will, slowly or rapidly, and the changes could be followed easily by measurements of conductivity, liminal values and pH.

Very frequently solutions of ferric acetate (3 per cent to 30 per cent) made up to dialyze and allowed to stand a few hours would gelatinize, and often freshly made solutions which were dialyzing over night against tap water for their first dialysis would be gelled the next morning. Theoretically it would have been possible to peptize these gels back to sols by adding the requisite amount of acid, but experience had shown that reversing the gelatinization involved such difficulties that it was not done, and instead all such solutions were thrown out and a fresh start made.

The procedure for preparing the sols follows:

A solution of ferric acetate was prepared by dissolving 200 grams of "Merck's iron acetate,* scales" in 800 cc. of distilled

* Analyses of these scales showed 32.4% of iron, 53.1% of acetate, and loss in weight after 30 hours of heating in an oven at 100° C. was 13.3%. This last per cent, however, was not constant, but grew larger as the sample was heated longer.

water. A mechanical stirrer was employed and the scales were added gradually in small amounts. When all the acetate was dissolved, the very dark red solution was poured at once into an 800 cc. collodion sack, and dialyzed against tap water over night. If the next day, the solution was still of the same fluidity and color (clear red) it was poured into a fresh sack and dialyzed against distilled water as described under Dialysis. But if, on the next day, the solution had turned into a light reddish gel, or had turned brown signifying that precipitation had begun, it was discarded.

1. Dialysis

(a) Preliminary Dialysis:

The preliminary dialysis lasted from 8 to 12 days, at the conclusion of which the sols were ready for experimentation, the actual time of dialysis varying in length from seven to thirteen hours per day.

The dialyzing vessel consisted of sacks made by pouring two coats of U.S.P.**X** collodion into Kjehdahl flasks of various sizes. For the preliminary dialysis, large sacks of 800 cc. capacity were employed.

During the first two days of the preliminary dialysis the distilled water in which the sacks were immersed was changed several times, and subsequently the water was changed once daily. The dialyzing was hastened by stirring with a jet of compressed air, which in this laboratory Hamburger had found was twelve times as efficient as without air. The air was purified by passing through two large tubes, one containing glass beads wet with sodium hydroxide and one containing glass wool wet with sulphuric acid, followed by cotton wool loosely packed to catch spray or dust. The air bubbling also speeded up the hydrolysis by removing acetic acid in the bubbles, since acetic acid in an aqueous solution has an appreciable vapor pressure.

The compressed air caused much troublesome foaming on the surface of the solution especially during the first two or three days, until most of the ferric acetate was dialyzed out.

During the first few days of the final dialysis the sacks occasionally had a distinct bluish color by reflected light, an unexplained phenomenon, but one which may possibly be due to adsorption of a thin layer of colloidal particles from the sol, thus being similar in nature to the adsorption of protein films on colloidion membranes as investigated by Hitchcock [8].

The outer solution (diffusate*) was tested daily for ferric iron with ammonium thiocyanate and hydrochloric acid and the test was always positive.

The level of liquid inside the sack was kept one or two inches higher than that of the distilled water outside, in order to avoid dilution of the sol. Another device used to secure the same end was to connect up the compressed air of three sacks in series which built up a pressure on the inside of the sacks.

Samples of the sol itself were tested for the presence of ferric iron. The tests were made on the supernatant liquid after sodium sulphate solution had been added to the sol in a liminal value test. All the tests were positive.

In both the above tests, the longer the dialysis, the fainter was the test for ferric iron.

If, during the dialysis a sample of the sol was desired for analysis or examination, it was drawn from the sack by detaching the compressed air rubber tube and blowing some sol up the glass tube down which the compressed air was ordinarily forced. This method avoided handling the sack, and having the sample contaminated with precipitated ferric oxide from the bottom of the sack.

Each evening when the compressed air in the laboratory was shut off, all dialyzing sacks were pulled up out of the water and suspended in air over night. Had they been left in the water, dialysis would have gone on and a precipitate of ferric oxide would have been deposited on the inner sur-

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* The practice among colloid chemists is to call what goes through the membrane the dialysate. Webster's dictionary, however, states that what goes through the membrane is the diffusate, and what remains behind is the dialysate.

face of the sack, thus preventing diffusion of ferric ions through the sack.

Suspending a sack of sol in air over night is really an ultrafilter set-up, water coming through the sack which results in slowly concentrating the sol. On one occasion an 800 cc. sack broke into 2½ liters of water in a battery jar, but the extra water was all ultrafiltered off by suspension in air in 4 sacks for several days.

When the preliminary dialysis was complete the sol was analyzed and stored in "Non-Sol" bottles in the dark [9]. These sols were used for aging and other experiments.

b. Final Dialysis.

Several sols were subjected to a second or final dialysis in order to discover at what point precipitation began. (See Incipient Precipitation).

2. Analytical Methods.

Iron was determined by the permanganate method [10] the samples being heated with sulphuric acid to white fumes before titration in order to drive off all acetic acid. The results are accurate to 0.2 per cent.

The first method tried to determine acetic acid in the sol was that given in Sherman's Organic Analysis (1917), page 129, namely, distilling with sulphuric acid and titrating the acetic acid distillate with sodium hyrdroxide. Phosphoric acid was also used in place of sulphuric acid but neither worked satisfactorily. Finally the method described below was used.

The acetic acid content was found by a direct titration method suggested by the procedure[11] employed for the determination of chromic oride in chrome tanning liquor. The method was as follows: Fifty cc. (more or less depending on the amount needed for a reasonable burette reading) of sol sample are pippetted into a seven inch white porcelain dish, and 400 cc. of distilled water added. One cc. of one per cent Phenolphthalein solution is added, also 50 grams of common salt, and the whole stirred and heated with two Bunsen burners. At once the titration is begun using 0.1N

(or 0.05N) sodium hydroxide which has been standardized with Bureau of Standards benzoic acid. A little less than the correct amount of alkali is added quickly and the solution is heated rapidly to the boiling point. After boiling the alkali is added a drop or two at a time cautiously until pink, when it is boiled a second time (which discharges the pink color) and more alkali added (one or two drops usually suffice) until pink around the edge of the dish. This is taken as the end-point. Near the end-point the precipitate of ferric hydroxide coagulates fairly well so that after stirring and waiting a minute or two, the hydroxide settles so that there is a wide margin of clear solution all the way around the edge of the dish, and in this margin the color change can be seen.

Heating increases the speed of hydrolysis of the ferric acetate (peptizing agent) producing acetic acid at a greater rate, while the salt squeezes out the last traces of the acetic acid as called for theoretically[12] and as has been proved experimentally[13].

Accurate results by this method are not always easy to obtain on account of difficulties arising out of the slow settling of the precipitate. The precision attainable was $\pm$ 1%.

III. TECHNIQUE

1. Liminal Values:

The term, liminal value, is defined as "the average in millimoles of that amount of sodium sulphate which just fails to precipitate and that amount which just does precipitate an equal volume of sol, under the conditions of the experiment."

The sol and the sodium sulphate solution were mixed in carefully cleaned tubes which were then centrifuged for two minutes, and the end-point was read off in accordance with the above definition to an accuracy of $\pm$ 5%.

The liminal values were interpreted as a measure of the stability of the sol.

2. Viscosity:

An Ostwald viscosimeter standardized against distilled water was employed. It was immersed in a water thermostat at 25.0° $\pm$ 0.1°. A 5 cc. sample of the sol was delivered into the viscosimeter from a standardized Mohr pipette and allowed to remain from ten to fifteen minutes in order to attain the temperature of the bath. The number of seconds outflow was observed with the aid of a stopwatch which read to one-fifth of a second. Each measurement was repeated five times and the average taken. The average deviation from the mean varied from 0.1 to 0.3 seconds.

Although there is a diversity of opinion as to the validity and significance of viscosity measurements for colloids, it seemed worth while to make the determinations for comparative purposes.

3. Surface Tension:

An improved duNoüy Tensiometer[14] was employed for the surface tension determinations. The instrument was adjusted so that it gave a direct reading of 73.0 dynes with freshly boiled distilled water on a carefully cleaned watch-glass at 22° C. The platinum ring was flamed before each new sol was read.

Since ferric acetate solutions foamed a great deal it was thought worth while to ascertain the surface tension of some

of the sols studied and the changes which they undergo on aging.

The changes in surface tension with aging are included in Table VI.

4. Conductivity:

The electrical conductivity of the sols was measured with a Wheatstone bridge arrangement using a circular slide wire, three variable air condensers, a Freas conductivity cell and a Vreeland oscillator manufactured by Leeds and Northrup. The cell containing the sol sample was immersed in a thermostat at $25° \pm 0.02°$. Three different resistances were used for each sol and two readings of each resistance were taken. Bright platinum electrodes were used instead of platinum black in order to avoid possible adsorption[1] of sol particles by the electrode. Before introducing a new sample into the conductivity cell, the cleaned cell was rinsed twice with small portions of the sol sample. As recommended by Morgan and Lammert[15] the cell was short-circuited except when being used for measurements.

The cell constant was determined with 0.01 N potassium chloride using Kraus and Parker's[16] specific conductivity value, 0.0012243. Successive measurements of the cell constant with fresh fillings of 0.01 N potassium chloride varied more than is customary with platinized electrodes. The maximum deviation of cell constants obtained was 3.8 per cent, while the average deviation was 1.4 per cent. The cause of these large discrepancies is unknown but is probably related in some way to the use of unplatinized electrodes. Parker[17] and Hamburger[3] using unplatinized electrodes report discrepancies of 2 per cent and 2½ per cent respectively. Parker observed that the discrepancy was largest where the resistance was small. The resistances obtainable with 0.01 N potassium chloride in this present investigation were only 300 ohms.

The experimental error, under the circumstances described above, is probably as much as 5 per cent.

The technique for pH determinations is described in the following chapter (IV).

IV. pH MEASUREMENTS WITH THE QUINHYDRONE ELECTRODE

Pauli and Matula[18], Frieden and Thomas[1] employed the hydrogen electrode to measure the hydrogen ion activities of their ferric oxychloride sols. Pauli and Matula working with electrodes saturated with hydrogen before immersing in the sol, found the pH of their sols equal to 7. Thomas and Frieden, working with sols dialyzed until they gave no test for ferric iron, obtained a pH of 4.9 while Browne[31] using a similar method, found for sols of purity 17.5 to 45.5 the pH equal to 7.

Ferric iron was found to be present in the ferric oxyacetate sols and in order to try to secure more accurate pH measurements in its presence the Quinhydrone method was tried out. This method as developed theoretically and experimentally by a number of chemists[20, 21, 22, 23, 24, 25, 26, 27, 28, 29], offers the advantage that it can be used in a number of cases where as Clark states, "the hydrogen of the hydrogen electrode is seriously attacked by one of the components of the solutions."

1. Theory

In the equilibrium between hydroquinone and quinone,

$$C_6H_4(OH)_2 \rightleftarrows H_2 + C_6H_4O_2 \quad - \quad - \quad - \quad - \quad (I)$$

the concentration of hydrogen has a perfectly definite magnitude which according to Biilman is $10^{-23.64}$ atmospheres at 25° C. This hydrogen pressure forms with the hydrogen ions of the solution a perfectly definite potential which can be determined by inserting a smooth platinum electrode, connected to a calomel electrode. The equilibrium is very soon attained which allows of measurements being made rapidly.

Since the reaction (I) above is reversible, the following equation is applicable at 25° C.,[29]

$$\pi = \pi_0 + \frac{0.059}{2} \log \frac{(C_6H_4O_2)}{(C_6H_4(OH)_2)} + 0.059 \log(H^+) \quad - \quad (II)$$

π is the potential observed, while π_0 is the normal potential of the system, viz., + 0.699 or 0.699 volts more positive than the normal hydrogen electrode.

When crystals of quinhydrone are dropped into an ordinary acid solution equal numbers of molecules of hydroquinone and quinone are formed, and this relationship is maintained constant under ordinary conditions, so that the second term of the equation involving these two substances drops out and we have

$$\pi = \pi_0 + 0.059 \log (H^+) \quad - \quad - \quad - \quad - \quad \text{(III)}$$

$$\text{or } \log \frac{1}{(H^+)} = pH = \frac{\pi_0 - \pi}{0.059} \quad - \quad - \quad - \quad \text{(IV)}$$

In using Equation IV for the calculations of this paper π_0 and 0.059 were corrected for temperature after the data given by Clark [29]. Also, it was necessary to add 246 millivolts, the basic value of the difference between the saturated calomel half-cell and the normal hydrogen electrode.

A supply of quinhydrone crystals was prepared by the method of Biilman and Lund (1921) as quoted by Clark [29].

The advantages of the quinhydrone electrode have been well summed up by Clark [27]: "One advantage of the quinhydrone electrode is the rapidity with which its equilibrium potential is obtained. Another advantage over the classic hydrogen electrode is this: The finely divided metal (platinum or palladium black) necessary to the operation of the hydrogen electrode is easily 'poisoned' by many substances or else will so catalyze the reduction of a substance as to alter the system under study. In the quinhydrone electrode, the hydrogen and the finely divided catalyst are elimniated. Its potential adjusts rapidly, very often much more rapidly than certain classes of reagents affect the constituents of the oxidation-reduction system. Consequently it is possible to use the quinhydrone electrode in solutions incompatible with the hydrogen electrode and even in systems which will ultimately oxidize hydroquinone."

2. Apparatus

The set-up used for the quinhydrone electrode was as follows: (1) Calomel cell with tubulure dipping into (2) a 30 cc.

beaker containing saturated potassium chloride; (3) a salt bridge connecting (2) and (4); (4) a 30 cc. beaker containing the sample of iron oxyacetate sol; and (5) a potentiometer.

The calomel cell was prepared with saturated potassium chloride solution. The 30 cc. beaker contained about 7 cc. of the sol being measured, into which dipped a platinum electrode, freshly gold-plated in order to attain equilibrium more quickly.

The potentiometer was a Leeds and Northrup, portable type. The working cell was tested frequently against the standard cell.

Salt bridges of various types were experimented with. First, an agar-agar bridge, suggested by Michaelis, was used. The contents of the tube in this case consisted of a saturated potassium chloride solution mixed with 5 to 10 per cent agar-agar, the mixture being warmed on a water bath and then allowed to cool to a firm jelly in the familiar double siphon bridge. This was used for the first series of experimental measurements. Sometimes, however, difficulty was experienced in having the jelly set properly, which circumstance led to the trial of a second method as follows: A collodion membrane was stretched across the mouth of the calomel cell fine bore bent tube (tubulure). The membrane rested on a glass plug which had been partly ground in as a stopper. The membrane was put in place by dropping a drop of collodion on the end of the tube and allowing it to dry somewhat before immersion in the ferric oxyacetate sol. As long as one kept the membrane in good condition by keeping it moist, it allowed fairly satisfactory readings to be made on the potentiometer, but it did not improve the tendency of the E. M. F. to drift (see next section, "The Cause of the Drift"). Moreover as pointed out by Fales and Stammelman[30] this membrane is subject to criticism from the standpoint of producing a "Donnan" effect, i. e., there is an equilibrium established between the diffusible ions on one side of the membrane and the diffusible ions (K and Cl) on the other. This would produce a potential difference which would interfere with the main E. M. F.

A round wooden toothpick was tried as a "junction membrane". After swelling by soaking it in water, it was carefully fitted into the mouth of the calomel cell tubulure, then the end of this tubulure was immersed directly into the sol sample and the measurement of E. M. F. made at once. This device apparently allowed potassium chloride to pass steadily through, as shown by the fall of E. M. F.

A fourth method tried was to use a ground glass stopper junction, a method previously used by several investigators[31]. The method consists in letting the liquids come into contact in the capillaries formed between the bearing surfaces of the ground-glass stopper and the ground tube. The results given in this paper were obtained with a double siphon tube and ground glass stopper kindly loaned by Dr. LaMer. Lamb and Larson[31] state that this junction is not constant or reproducible to more than 0.2 or 0.4 millivolts, but LaMer and Baker[31] secured more constant results than that. The double siphon ground glass stoppered bridge used for all the measurements in this paper, except the first series, had an addition made to it during the preliminary experiments, namely, both arms were made the same length. This alteration was made in order to avoid hydrostatic pressure downward on the longer arm at the bottom of which the stopper had been ground in. This downward pressure observed before the arms were equalized resulted in saturated potassium chloride forcing its way down into the sol where it caused the sol which it touched to precipitate slowly and the E. M. F. was lowered.

To further restrict the flow of potassium chloride through the ground glass capillaries a very small amount of stop-cock grease was spread on three-quarters of the circumference of the stop-cock. This method resulted in readings which showed a minimum of drift, about one millivolt in ten minutes.

3. The Cause of the Drift.

The writer studied the effect on drift of allowing three different amounts of saturated potassium chloride to come in contact with the sol: (1) successive drops of KCl; (2) less KCl; (3) still less KCl as noted below:

(1) A series of measurements were made with the quinhydrone electrode using S27 in which successive drops of saturated potassium chloride were added to the sol. The apparatus was set up in the regular way using the ground glass stopper junctions. The results were as follows:

Total Volume of KCl Solution Added	E.M.F.
0	0.198 volts
0.04 cc.	0.180 "
0.08 cc.	0.171 "
0.12 cc.	0.167 "

(2) In the early experiments a toothpick, which had not been previously soaked in water, was used in place of the agar bridge. Later, one was used which had been soaked in water to swell the wood and therefore fill the interstices between the glass and the wood. In both cases, a small amount of potassium chloride came through the calomel cell tube into the sol. The E. M. F. drop was 2.5 millivolts in 8 minutes.

(3) The use of the ground glass stopper as described on page 19 illustrates the third case where only a very little potassium chloride could possibly leak in. Two typical observations showing the effect of time are shown below:

Time from Start	E.M.F.
(a) 0 minutes	0.2675 volts
8 minutes	0.267 volts
(b) 0 minutes	0.267 volts
25 minutes	0.265 volts

From a study of the results in (1), (2) and (3) it is evident that there is a relation between the amount of electrolyte, potassium chloride, which is allowed to flow into the iron oxyacetate sol and the amount of the lowering of the E. M. F. The relationship found is this: The greater the amount of electrolyte, potassium chloride, allowed to flow into the iron oxyacetate sol, the greater the lowering of the E. M. F.

The mechanism of this effect is not clear, but some considerations may be set forth.

The change in activity of the hydrogen ion when a salt is introduced into the solution ("salt-effect") was considsidered. But the concentration of potassium chloride in the sol even when three drops of saturated potassium chloride are introduced is not sufficient to provide 0.2 M potassium chloride and this is the lowest concentration which Sorensen and co-workers[32] state will produce a change in H-ion activity in the acid solutions (e. g. 0.01 N Hydrochloric acid) which they used. In the experiments described above, however, we are dealing with different components and a different type of solution from those experimented with by Sorensen so that the effect, if it is an effect on the H-ion activity, might well be quite different. This clue was not, however, followed further.

Another type of explanation has been considered. According to Duclaux's theory[33] the micelle would consist of $(Fe_2O_3)x\ (FeAc_3)y$; or $(FeOAc)\ x\ (FeAc)_3$, and the added potassium chloride would react with ferric acetate as follows:

$$\begin{array}{l} FeAc_3 \rightleftarrows Fe^{+++} + 3Ac^- + 3H_2O \rightleftarrows 3HAc + 3OH^- \\ 3KCl \rightleftarrows 3Cl^- \quad 3K^+ \\ \qquad\quad \uparrow\downarrow \quad\ \uparrow\downarrow \\ \qquad\quad FeCl_3 \quad 3KAc \end{array}$$

Theoretically these reactions would go forward because of the formation of unionized acetic acid. This would cause an increase of OH concentration, corresponding to a larger pH value which is what is obtained experimentally.

Concomitant with the above reaction there would also be a precipitation of iron particles which had been "peptized" by the ferric acetate. This precipitation would take place as soon as the concentration of the potassium chloride exceeded the "liminal value." Such a precipitate was observed in the neighborhood of the drop when saturated potassium chloride was dropped into the solution.

4. Accuracy.

Since the downward drift in potential was persistent the question arose as to what reading of the E. M. F. should be considered as representing a condition of equilibrium between the electrode and the ratio (quinone to hydroquinone=1).

To answer this question, experiments were set up to discover how long after quinhydrone had been added was required for the potential to become constant. Three 30 cc. beakers were prepared and to each was added 7 cc. of sol and 20 mg. quinhydrone. These beakers were left exposed to the air as in an ordinary measurement, and after different intervals of time, the gold-plated electrode was put into the sol and the potential measured. The results were as follows at 21° C:

Minutes quinhydrone was in sol before measuring	E.M.F. millivolts	pH
2	204	4.37
6.5	203	4.39
30	201	4.42

The results show that equilibrium is not reached with time up to one-half hour, for the potential falls here where the electrode and ground glass junction are not kept in the sol at about the same rate, one millivolt for 10 minutes, as it does when they are kept in the sol. In other words, this drop of one millivolt in 10 minutes appears to be identical with the drift discussed in the previous section.

Since all investigators whose papers were examined report that equilibrium with the quinhydrone electrode is quickly established as a rule, the writer decided to use the first and highest value of the E. M. F. for calculating pH on the assumption that the drift is due to some slow secondary reaction, not understood at present. Clark and Cohen[34] found frequently that after a downward drift of several minutes, the E. M. F. was constant for several more minutes, giving them a plateau on their curve, then the E. M. F. fell away again downwards. When there was a plateau they chose

this for the point of equilibrium and used that value for their calculation. When there was no plateau they used the initial reading.

Moreover as one can observe in the results given above, a change of 3 millivolts (from 204 to 201) makes a difference of only 0.05 (4.42-4.37) in pH.

Several readings of the E. M. F. of S27 were made at intervals during eight days and the extreme fluctuation was 4 millivolts. If we assume that the fluctuation might be as much as 6 millivolts (a liberal allowance) this would make a difference of 0.1 pH and the extreme variation on either side of the mean would correspond with a precision of $\pm$ 0.05 pH.

5. Results.

pH measurements are given in connection with Aging at Elevated Temperature, (Tables IV, V, VI, VII) and in the Table of Comparison of pH Values of Various Iron Oxide Sols (Table I).

Comparison of pH values of Various Ferric Oxide Sols

Every sol measured and compared (see Table I) has a pH on the acid side, a result which is in harmony with the hydrolytic viewpoint (discussed later).

Sols No. 3 and 4 each having a total iron content of 415 millimoles per liter are observed to have distinctly different pH values, the oxybromide sol being more acid. Since hydrochloric and hydrobromic acids of equal concentration have practically the same hydrogen ion concentration this difference shows that ferric oxybromide micelles hydrolyze to a greater extent than ferric oxychloride micelles.

The two chloride sols (Nos. 2 and 3) although prepared by two entirely different methods show practically the same acidity.

TABLE I.

COMPARISON OF pH VALUES OF VARIOUS FERRIC OXIDE SOLS.

No.	Experimenter	Description of Sol	Iron Content–milli–equiv. per L.	Ratio Equivs. Fe to Equivs. halide or acetate	pH	Remarks
1	Frieden[2]	Ferric Oxychloride (ferric oxide peptized by ferric chloride)	Various Concentrations		4.9	4.9 is the mean of several "pure" hydrosols of various concentrations.
2	Hamburger*	Ferric oxychloride (C16) a Graham sol, age= 1 year	440	22.4	3.9	Nearly the same pH as the other Graham sol (4.1)
3	"	Ferric oxychloride by Neidle's method, age=6 mo.	415	24.0	4.1	Sol prepared by same method as Br.44
4	"	Ferric oxybromide (Br44) by Neidle's method, age=7 mo.	415	20.4	2.7	Sol prepared by oxidizing $FeBr_2$ to $FeBr_3$ with H_2O_2
5	"	Iodine Sol, age=2 years, 1 mo.	Not analyzed		1.9	Prepared by heating iodine and iron filings. Dialyzed 3 days only.
6	Mabee	S31	357	12.8	4.8	
7	"	S22	555	13.8	4.2	
8	"	S27	567	12.0	4.3	

* Sols prepared by Hamburger and pH values subsequently measured by the writer. Cf. Hamburger's Dissertation, Columbia University, p. 27 (1926).

V. EXPERIMENTAL

A. Incipient Precipitation.

Frieden[1] discovered that when he dialyzed ferric oxychloride sols until precipitation began, the precipitation ratio or "purity" was always the same value at that point. It was decided to dialyze the ferric oxyacetate sols to discover whether a similar ratio held.

Therefore Sol No. 22 (hereafter called S22) which had already been subjected to a preliminary dialysis was used to prepare sols of varying concentration (See Table II). These were put into small collodion sacks and the final dialysis begun, the contents being stirred by compressed air. The smaller sacks provided a large surface compared to the volume of sol which would tend to speed up dialysis.

In the early experiments the outer solution was tested daily for the presence of ferric iron with thiocyanate, for it was hoped that, if dialysis were continued long enough, a negative test would be obtained. If we assume that as a molecule of ferric acetate is used up, all the iron goes into a colloidal particle (or into an agglomerate of colloidal particles eventually forming a precipitate) then a negative test for iron would mean that all the ferric acetate had been hydrolyzed. This test, however, always gave positive results, and although the test showed a constantly diminishing amount of iron, the sol gelled before a negative test was obtained.

Careful observation of the contents of each sack was made daily as to (1) appearance by transmitted light and by (2) reflected light; (3) formation of precipitation on the bottom, (4) whether or not there was turbidity when a sample was viewed in a small glass tube by transmitted light.

The changes which took place during the final dialysis may be summarized as follows:

	At the beginning	At incipience of precipitation
Appearance of sol in sack by transmitted light	For concentrated sols —dark red;	Red (turbidity difficult to discover)
Appearance by transmitted light in small glass tube	For dilute sols— light red.	Light red and turbid
Appearance by reflected light	Black	Chocolate brown and opaque
Appearance on bottom of sack	No precipitate	Cloudy brown precipitate of ferric hydroxide (small amount)

When the criteria above indicated that precipitation had begun, dialysis was stopped, the sols were centrifuged and the supernatant liquid analyzed. The results with S22 are shown in Table II.

In this paper the " purity" or ratio or precipitation ratio is defined as the ratio of equivalents of total iron to equivalents of total acetate in the sol, or in the supernatant liquid above the precipitate.

TABLE II.

CONCENTRATION AND RATIOS OF SOLS AT INCIPIENCE OF PRECIPITATION. EFFECT OF DILUTION.

S22. 556 milli-equivalents Fe per Liter. Ratio: 14.

Sol. No.	Dilution	Duration of Dialysis Preliminary Hrs.(days)†	Final Hrs.(days)	Analysis after Dialysis Equivs. Fe per Liter	Eqvs. Ac. per Liter	Ratio Eqvs. Fe. to Equivs. Ac.
S22[x]	none	109 (9)	98 (10)	0.515	0.0236	22
S22[a]	1 : 1	105 (9)	105 (11)	0.389*	0.0169	23
S22[b]	1 : 19	105 (9)	119 (12)	0.159*	0.00636	25

* The values for iron appear high when one observes the dilution to which these sols were subjected before the final dialysis. This is caused chiefly by the ultra-filtration to which each sack was subjected during dialysis.

† Days refer to total elapsed time while the hours signify actual time of dialysis the sol being in an "ultrafilter" position the balance of the time. See page 12.

S22^{x} is the original stock sol, subjected to a second and final dialysis. S22^{a} is the original sol diluted with an equal volume of distilled water, while S22^{b} is the original sol diluted with 19 parts of distilled water.

A duplicate series of tests on the precipitation ratio was undertaken with Sol 24 and the results are shown in Table III.

TABLE III.

EFFECT OF DILUTION. CONCENTRATION AND RATIOS OF SOLS AT INCIPIENCE OF PRECIPITATION.

S24. 571 milli-equivalents Fe per Liter. Ratio: 15.

Sol. No.	Dilution	Duration of Dialysis: Preliminary Hrs.(days)	Duration of Dialysis: Final Hrs.(days)	Analysis after Dialysis: Equivs. Fe per Liter	Analysis after Dialysis: Eqvs. Ac. per Liter	Ratio: Eqvs. Fe. to Equivs. Ac.
S24^{x}	none	140 (13)	147 (13)	0.228	0.0111	21
S24^{a}	1 : 1	140 (13)	137 (13)	0.202	0.0941	21
S24^{b}	1 : 4	140 (13)	99 (10)	0.0769	0.00389	20
S24^{c}	1 : 19	140 (13)	66 (6)	0.0202	0.00112	18

S24 is the original stock sol. S24^{x} is the original stock sol subjected to a second and final dialysis. The other three sols were diluted with distilled water as shown.

Considering the results in the last column of Tables II and III it is seen that the values for the precipitation ratio range from 18 to 25. This wide range is due to the difficulty of judging exactly when precipitation begins. The results in Table III were secured after more experience had been gained and are subject to less error. The average of the last four ratios of Table III is 20 ± 1. We may conclude, therefore, that ferric oxyacetate sols, irrespective of concentration, begin to precipitate out when they reach a precipitation ratio of approximately 20.

This result means that the ferric oxyacetate sol remains stable as long as the ratio of equivalents of total Fe to equivalents of acetate is no greater than approximately 20. But if, by continued dialysis, the ratio becomes greater than approximately 20, then the sol becomes unstable and begins to precipitate.

In comparison with the above value of 20, Frieden[2] found the value of 43, this result being obtained if his molar ratio, 21, is re-calculated to equivalents as used in the present paper. Hence Frieden's discovery that iron oxychloride sols exhibit a fairly constant incipient precipitation ratio is paralleled in the case of iron oxyacetate sols.

Hamburger endeavored to obtain a similar precipitation ratio for ferric oxybromide sols, but unexpectedly, the values obtained were not constant. The values which were obtained, however, were all considerably higher than 43, which is reasonable since, in general, the molar solubilities of soluble "crystallized" bromides are higher than those of the chlorides and since "if the solution link theory is true, we should expect the greater solubility forces of the bromide connecting link to hold more complex ferric cation in solution than the chloride" (Hamburger's dissertation),

Additional confirmatory evidence is presented in Table III which discounts the charge theory of the stability of colloids.

The charge theory accounts for the stability of inorganic colloidal micelles on the basis of the principle that like bodies repel one another and that the repulsive forces thus developed are greater than the forces of mutual attraction.

According to this theory the more concentrated the sol the greater the electrical charge needed on the surface of the micelles in order to overcome the greater attractive force of the micelles being crowded together. The greater electrical charge could be furnished by more ferric ions being adsorbed on the surface of the micelle, but this condition, if true, would evidence itself by having a smaller limiting ratio at precipitation. The fact is, however, that the ratio is the same no matter what the concentration of the sol. Hence instead of the charge being the predominant factor for stability, we see that this rôle is played by ferric acetate as stabilizing agent.

The "stabilizing agent" (or peptizer or solution-link) functions by exerting a force of attraction between the micelle to which it is attached on the one hand and the water solvent in which it is soluble on the other hand ("homologating ef-

fect"). As the stabilizing agent is gradually removed by hydrolysis, eventually a point is reached (ratio: 20) when there is not enough stabilizing agent present to exert sufficient force to maintain the micelle in solution, whereupon precipitation follows.

The micelle in this case may be defined according to the viewpoint developed by Duclaux[33], Wintgen and Blitz[35], Lottermoser[36] and Pauli and associates[37] as a particle consisting of iron, oxygen, hydrogen and the acetate radicle with a positive charge, due probably to the adsorbed (or associated) ferric ions, there being in the intermicellary liquid surrounding the particle, sufficient acetate ions to balance the electrical charges of the adsorbed ferric ions. The exact manner of combination of the four constituents of the micelle is not known, but that they are present in the corresponding case of the Graham sol was shown by Pauli and associates[37]. Also the manner of association of the ferric acetate with the particle is not definitely known, but the theoretical picture glimpsed in the definition, if true, would account satisfactorily for both electrophoresis and stability.

Recent interest has centered a good deal on the stabilizing agent for as McBain says[38] "it is not the nature of the interior, but the composition of the exterior of the particle which determines its chief properties and degree of stability. Probably in every case the exterior has to consist of a stabilizing agent."

B. Aging Experiments.

To accelerate the changes[39] which these sols undergo in time, several aging experiments were conducted at 90° C.

In each experiment about 800 cc. of the sol were poured into a one liter round bottom Pyrex flask. The rubber stopper was securely tied down with stout cord in order to withstand the high vapor pressure developed in a closed system at high temperature and the flask was then put on a Sorbite ring in an electrical oven at 90° C. (± 1°). The object of using one large flask instead of several small ones was so that all the sol used for sample should have exactly the same heat treatment.

Observations of the appearance of the sol were made from time to time in order to correlate changes in appearance with the changing values of the measurements mentioned below.

Samples were taken at various intervals by pouring from the large flask into a "Non-Sol" bottle. The large flask was immediately stoppered and replaced in the oven. The samples were allowed to stand at least twenty-four hours* and as soon after that as feasible, small portions were pippetted out and three or more of the following measurements were made: (1) liminal value; (2) viscosity; (3) surface tension; (4) conductivity; (5) pH.

The results of the first aging experiment at 90° C are given in Table IV below and in Figure I (Curves marked I). The age of each sol at the start of its use for aging is recorded because, as was observed in the case of aging at room temperature, slow changes in properties take place when sols stand in bottles in the laboratory and therefore the age must be taken into account in general and, particularly when comparing different measurements on the same sol which were measured at different time-intervals from the completion of the preliminary dialysis.

Table IV shows that the pH drops steadily with time, signifying an increasing acidity, as would be expected on the assumption that hydrolysis of the "stabilizing agent" ferric acetate, is taking place.

Increase in conductivity is shown as would be expected from the decrease in pH. The decrease in liminal values can be accounted for in this way: As hydrolysis proceeds, the "stabilizing agent" or "solution link," (ferric acetate) is progressively removed, which decreases the stability of the sol, hence less electrolyte (sodium sulphate) is needed for precipitation. The same theory will explain the decrease of viscosity (107.4 to 97.7), for, as the micelles become more and more unstable, the attractive forces predominate, presumably they gradually form aggregates which later, when large enough,

* Thereby coming to laboratory temperature, and securing constancy of conditions for all measurements.

TABLE IV.

Aging Experiment Elevated Temperature (90° C.) - - (I)

S27. 567 milli-equivalents Fe per liter. Ratio=12.0. Age of sol=one month.

Sample No.	Time from Start Hours	Time from Start Days	Na_2SO_4 Liminal Value	Viscosity (seconds) H_2O=85.5 seconds	Conductivity (mhos) $\times 10^{-4}$	pH	Appearance
1	0		1.7	107.4	1.26	4.3	Dark brown red by transmitted light. Very dark brown practically black by reflected light.
2	5		1.5	101.7	1.42	4.2	About the same.
3	28		1.1	99.0	2.31	3.9	Browner than at zero time by reflected light, turbid. Slight white precipitate on bottom.
4		3	1.0	97.7	2.79	3.4	Mostly brown by transmitted light. Light chocolate brown by reflected light, turbid.
5		7	.73	99.3	2.94	3.5	More white precipitate than in No. 3. Part of sol had gelatinzed. Jelly seen on walls of flask.
6		23	.67	214.8	3.40	3.3	Still more precipitate than in No. 5. Very light chocolate brown and turbid.

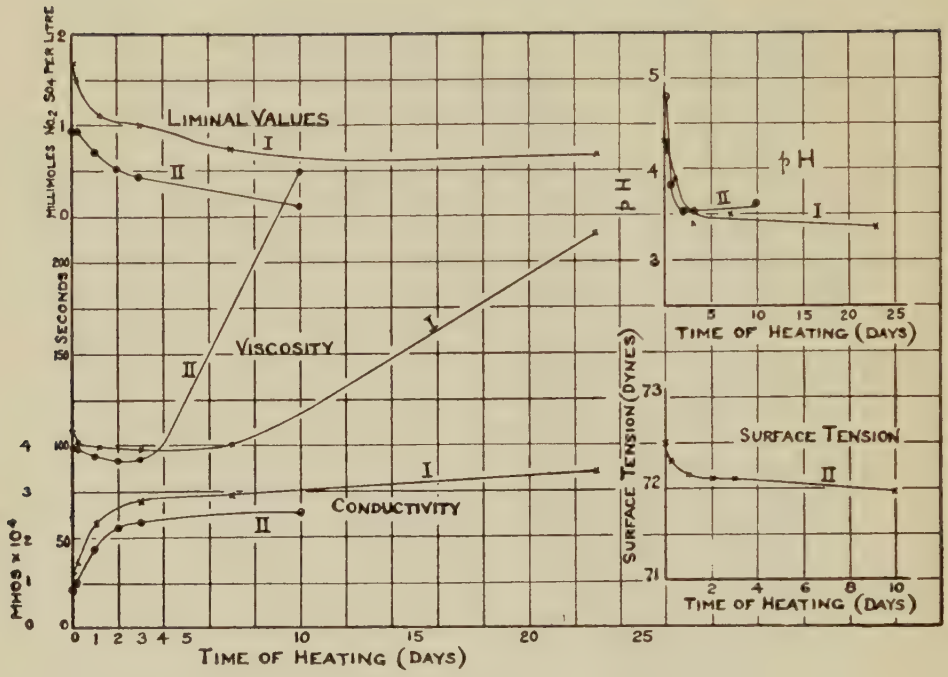

FIGURE I.

AGING EXPERIMENTS

I—S27 (Cf. Table IV). Fe 567 milli-equivs per liter; ratio=12.0
II—S31 (Cf. Table V). Fe 357 milli-equivs per liter; ratio=12.8

precipitate and the more they aggregate the more the intermicellary liquid approaches the consistency of water, hence the drop toward the viscosity of water. The rise to 99.3 and 214.8 is explained by the fact that the sol gelled rapidly so that the plastic flow of a gel instead of the viscosity of a sol was being measured.

A second aging experiment was conducted in which the concentration of iron was smaller than in the first while the ratio, 12.8 remained practically the same. Since in the first experiment it was observed that most of the changes occurred

in the first seven days, the aging period of the second was reduced to ten days. The results are shown in Table V and Fig. 1 (See curves marked II), in which are included also some surface tension measurements.

The first four curves of the second aging experiment agree in general with the corresponding curves of the first. Concerning the curve for surface tension it is to be noted that the initial value, 72.5, is lower than that for water, as would be expected since ferric acetate lowers the surface tension. The fall in values with aging is reasonable on the basis of the hydrolytic viewpoint, for increasing amounts of acetic acid would cause progressive decrease of surface tension.

The results of a third aging experiment are given in Table VI and Figure 2. Two additional variables were introduced into this experiment. The first was dilution—sol B is half as concentrated as A; and the results are what would be expected for all three of the measurements. The liminal value of B starts with 1.32 and the decrease to 0.82 and on down to 0.38 is more rapid than with the concentrated sol, and is reasonable for hydrolysis goes farther in dilute solutions.

The conductivity of A increases to more than twice its value at the start as is also the case in aging experiment 1 where the iron concentration and ratio are about the same. But C with its added acetic acid at the start has a higher conductivity (2.4) to start with, but does not increase to more than about one and one-half times the original value.

If the increase in conductivity is due chiefly to increase of H ions from hydrolysis, the results would be reasonable because the pH of C was found to decrease from 3.4 to 3.2 which corresponds to a change in concentration from .0004 to .00063 moles of H ion, i. e., about one and a half times.

The second variable introduced was acidity. Acetic acid was added to Sol C so that its pH at the start was 3.4. The numerical decrease in pH (0.2) for C produced by ten days of aging is small compared to that for A (0.9) and B (0.7) but is to be expected since the added acid would tend to establish the hydrolytic equilibrium.

TABLE V.

Aging Experiment at Elevated Temperature (90° C.) - - (II)

S31. 358 milli-equivs. iron per liter. Ratio=12.8. Age of sol=one month.

Sample No.	Time from start	Viscosity (seconds) H_2O=85.5 seconds	Na_2SO_4 Liminal values	Conductivity (mhos) $\times 10^{-4}$	Surface Tension (dynes)	pH	Appearance
1	0	98.7	0.95	0.85	72.5	4.8	Dark red by transmitted light. Very dark brown, practically black by reflected light.
2	4 hrs.	98.3	0.95	0.97	73.3	4.8	Same.
3	1 day	92.7	0.70	1.7	72.15	3.8	Somewhat more brown by reflected light than No. 1.
4	2 days	92.3	0.50	2.2	72.10	3.5	Dark brown red by transmitted light. More brown than No. 3 by reflected light, choc. brown, turbid.
5	3 days	93.8	0.43	2.3	72.10	3.5	Dark brown red by transmitted light, chocolate brown by reflected light, turbid. Noticed piece of jelly on edge of liquid.
6	10 days	248.6	0.10*	2.5	71.95	3.6†	Dark brown by transmitted light. Very light choc. brown by reflected light, turbid. Amount jelly increased.

* Value uncertain as sample 6 was not homogeneous.

† Value obtained with a collodion tip bridge and hence not so reliable as the other pH values but indicates approximately that the pH value at the end of 10 days was not much different from that at the end of 3 days (3.5).

TABLE VI.

Aging Experiments at Elevated Temperature (90° C.) - - (III)

S22 { A. Concentrated stock sol (total vol. 495 cc.) Fe=555 milliequivs per liter. Ratio=13, pH=4.2
S22 { B. S22 diluted 1 : 1 (total volume 450 cc.)
S22 { C. 225 cc. of S22 plus 225 cc. of an acetic acid solution to make pH of mixture 3.4. Age of S22, 8 months.

Sample No.	Time from Start (days)	Na_2SO_4 Liminal Values	Conductivity mhos×10^{-4}	pH	Appearance by transmitted light	Appearance by reflected light
1A	0	2.0	1.83	4.2	Dark red	Very dark brown
1B		1.32	1.17	3.9	" "	" " "
1C		1.57	2.4	3.4	" "	" " "
2A	1	1.5	3.09	3.4	Dark brown red	Distinctly brown
2B		0.82	2.19	3.5	" " "	" "
2C		.93	4.1	3.2	Dark red	Brown
3A	2	1.32	3.55	3.2		
3B		0.60	2.31	3.4		
3C		.73	4.2	3.2		
4A	3	1.15	3.67	3.3		
4B		0.55	2.42	3.4		
4C		.70	4.3	3.2		
5A	6	1.07	3.87	3.3		
5B		0.45	2.57	3.4		
5C		.55	4.1	3.2		
6A	10	1.00	4.04	3.3	Some ppt. on bottom	Chocolate brown—turbid
6B		0.38	2.76	3.2	" " " "	" " "
6C		.42	3.8	3.2	No " " "	Much less turbid than A & B.

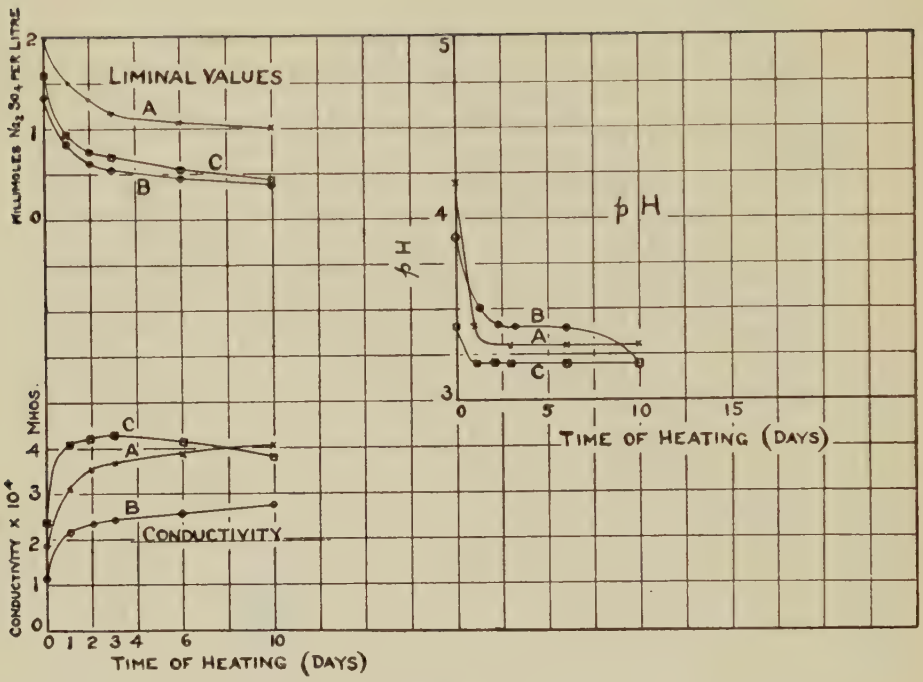

FIGURE 2.

AGING EXPERIMENT III

S22 (Cf. Table VI) Fe=555 milliequivs/L; ratio=13.8

In order to check the results of Table VI use was made of a small amount of B and C sols which remained over from aging experiment III in a new experiment IV (See Table VII). The remaining 35 cc. of B were not altered at all, but the remaining 35 cc. of C were mixed with an additional amount of acetic acid so as to reduce the pH to 3.2. The purpose of this alteration was to begin with the same pH with which sol C ended in Experiment III in the hope that the higher H ion concentration would effectively prevent any hydrolysis whatsoever. As shown in Table VII the final measurement showed no increase in acidity but rather a slight decrease.

TABLE VII

Comparison of Two Aging Experiments at Elevated Temperature (90° C.)

Aging Experiments III* and IV

Aging IV B_1—identical with B of Aging III. Total volume 35 cc.
C_1—identical with C of Aging III except that acetic acid was added to 25 cc. of C to change the pH from 3.4 to 3.2

Aging III (transcribed from Table VI)					Aging IV			
	Sample No.	Time from start (days)	Na_2SO_4 Liminal Values	pH	Sample No.	Na_2SO_4 Liminal Values	pH	Appearance
1	B	0	1.32	3.9	B_1	1.32	3.9	Very dark brown by reflected light
	C	0	1.57	3.4	C_1	(3)	3.2	Dark red by transmitted light.
2	B	10	0.38	3.2	B_1	0.10†	3.7†	Light chocolate brown, more than C by reflected light.
	C	10	0.42	3.2	C_1	0.33	3.3	Chocolate brown, no precipitation on bottom, no jelly.

* See Table VI.

† Sol had gelled which would influence result of B_1. B did not gell at all.

(3) The liminal value for C_1 not determined as amount of sol was insufficient.

Note: The two values given for B_1 are identical with those given for B, and the two sols are identical except that B_1 sol was one month older than B when the heating began.

The liminal value (0.10) of Sample B_1 (Table VII) is considerably lower than that of B (o.38) which would be accounted for by the fact that B had gelled a good deal during the heating.

With both C and C_1 sols the acetic acid added completely prevented precipitation and kept the two sols comparatively clear, a result entirely in accord with the hydrolytic viewpoint.

In general, the aging experiments agree with each other (Cf. Figs. 1 and 2) and show that as the time of heating increases, i.e., as hydrolysis progresses, the liminal values decrease, the conductivity increases and the pH decreases, all of which are to be expected if the effect of heating is simply, as pointed out in connection with Table IV the promotion of rapid hydrolysis of the stabilizing agent, ferric acetate, with consequent production of acetic acid.

The liminal value curve falls rapidly during the first two days, because the 70 degrees rise of temperature (i. e., from 20 to 90) would greatly speed up hydrolysis thus altering a large proportion of the stabilizing ferric acetate. The same reasoning accounts for the first steep portion of the other curves.

On one occasion a small amount of sol was left in the oven at 90° C. for a period of three or four months. At the end of that time the sol had precipitated out leaving a water white supernatant liquid. Evidently, therefore, the liminal value curve slowly approaches zero.

In addition to the discussion of the third aging experiment following Table VI it should be noted that three curves for Sol A (concentrated sol) resemble the curves of Figure 1 as they should. Curves (B), (a diluted sol) and (C) (with added acid) show the changes in behavior called for by the theory of hydrolysis.

Further there is a general correspondence between the form of the liminal value curves which measure stability and the conductivity and pH curves, the two latter being clearly dependent on the stage of hydrolytic equilibrium.

Of particular value is the fact that in aging experiments 1, 3, and 4 the pH of all the sols approaches a constant value

in the neighborhood of 3.2. In other words, these sols whether concentrated, or diluted 1 to 1 or with acetic acid added, all reached a state of equilibrium at a pH of approximately 3.2.

In general then, it may be concluded that the results obtained with liminal values, conductivity and pH and the general correspondence between the liminal values and the two latter, furnishes strong confirmation of the conclusion arrived at in a recent dissertation[3] from this laboratory, namely, a sol of this type should be defined by its stage of hydrolytic equilibrium as well as by the amount of constituents present.

Aging Experiments at Room Temperature

It was observed that all the ferric oxyacetate sols when put away in Non-Sol bottles for storage began at once to precipitate out fine yellow particles on the bottom of the bottle. This deposit of iron oxide particles increased in size very slowly as time went on.

In the case of ferric oxybromide sols, Hamburger[3] did not notice any precipitation till after six months. A Graham sol (ferric oxychloride) prepared in this laboratory was stable for approximately six years when it began to precipitate.

In order to study the relative velocity of changes going on in the sol at 90° C. and at laboratory temperature, the following measurements at different time intervals were made on S27 kept at laboratory temperature: liminal value, viscosity, conductivity, and pH. The pH decreased from 4.5 to 4.2 in 80 days. The viscosity decreased from 107.4 to 106.4 seconds in 165 days while the conductivity increased from 1.26×10^{-4} to 1.51×10^{-4} mhos in 167 days. The liminal value decreased from 1.7 to 1.4 millimoles sodium sulphate per liter in 240 days. All these changes with time are similar in direction to those found at elevated temperatures, although the magnitudes are, of course, less on account of the lower temperature. These results confirm those obtained at elevated temperatures.

VI. DISCUSSION

The data of this paper relating to removal of the "stabilizing agent" by hydrolysis indicate that the nature of the hydrolysis is progressive. The specific data were as follows: the decreasing pH, increasing conductivity, the decreasing stability, together with the very gradual increase in the amount of fine precipitate on the bottom of the "Non-Sol" storage bottles which was observed from the close of the preliminary dialysis.

The nature of the "progressive hydrolysis" has been studied by several investigators. Neidle[40] believes that clear ferric oxide hydrosols containing ferric ion contain an oxychloride of definite composition whose ratio is 20 equivalents of ferric iron to one of chlorine. This oxychloride is a colloidal particle and enters into a series of hydrolytic equilibria. The writer prefers the view of Hamburger[3] notwithstanding the criticism of Weiser[41] on hypotheses of this type. According to this view, the hydrolysis in the case of ferric oxyacetate would be represented as follows:

$$(\text{iron complex})\ Ac_x + yH_2O \rightleftarrows (\text{iron complex})\ Ac_{x-y} + y(OH) + yH\,Ac$$

The iron complex would consist of Fe, O, H, $C_2H_3O_2$ radicle combined in some way not known at present, possibly as $xFeO.yFe(C_2H_3O_2)_3.z\ H_2O$ or as $xFeOAc.yH_2O$. This complex is associated with the acetate radicle and the total particle resembles an electrolyte. On hydrolysis the negative acetate ion becomes combined with the hydrogen ion from water, forming acetic acid, part of which on dialysis goes through the membrane into the diffusate. The undissociated acetate remains adhering (adsorbed) to the outside of the complex, the whole constituting the micelle according to Duclaux's view. The OH radicle presumably combines with iron in the micelle forming ferric hydroxide.

The continued loss of acetate as hydrolysis progresses, and the entrance of OH into the micelle involving a re-arrangement decreases the stability of the micelle (as already pointed out

above in connection with the charge theory) "resulting in greater attractive forces between particles leading to aggregation until finally that degree of aggregation is reached at which precipitation occurs."

This hypothesis of "progressive hydrolysis" accounts satisfactorily for the data presented in this paper.

VII. SUMMARY

1. Iron oxyacetate hydrosols of varying iron content and ratio have been prepared and studied by means of experiments on dialysis, aging and pH determinations. The study is the first of its kind known to have been made on this sol.

2. It has been shown that when iron oxyacetate sols of different concentration are dialyzed, incipience of prcipitation begins when the ratio of equivalents of iron to equivalents of acetate is approximately 20. In other words, when the sols are "impure" and have ratios less than 20, they are stable but sols whose ratio or "purity" exceeds 20 are unstable.

3. Evidence has been presented in support of the theory that the stability of the micelle is due to a stabilizing agent (solution-link theory).

4. The quinhydrone method for pH determination has been applied to various iron oxide sols.

5 The pH values of oxychloride, oxybromide, oxyiodide and oxyacetate sols are all on the acid side, a fact which is in harmony with the hydrolytic definition of these sols.

6. Ferric oxyacetate sols when aged show a decreased stability, an increased conductivity and an increased acidity.

7. Sols should be defined, not only by the amount of constituents present, but also by their stage of hydrolytic equilibrium.

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